ION EXCHANGE AND INCREASING THE STRENGTH OF GLASS

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ABSTRACT: The stress coefficients in glass resulting from ion exchange were determined and calculated.

The essential mechanism of ion exchange consists in the exchange of a sodium /2029*
ion in glass for a lithium ion of the melt. This causes a decrease in the coefficient of linear thermal expansion (c.l.t.e.) in the modified surface layers, thus producing compressional stress and expansional stress in the inner layers. The magnitude of these stresses may vary and would depend on several factors.

The stress of ordinary sheet glass** after treatment in lithium layers was determined by the method of gradual grinding off [1], adapted for application to glass [2].

The samples, used for the measurements, had dimensions of 120 x 25 x 3.5 mm; they were treated in lithium salts for 1 hr at 580°C. The thickness of the ion exchange layer under these conditions reached 180-200 nm, and the thickness of the initially removed layers*** did not exceed 10 nm.

Stress was calculated by an equation presented in paper [2]. A diagram of compressional stress coefficients was based on the data obtained (Fig. 1, curve 1). The maximum stress was reached on the surface (3.5-3.8 kg/mm^2).

The samples were not annealed after treatment in the melt, because this would have caused the redistribution of diffusion conditions. The contribution of tempering stresses was evaluated on samples which were correspondingly treated, but not immersed into the melt. The stress diagram for this case is shown in curve 2 of Figure 1. These stresses are small and do not significantly affect the hardening upon ion exchange.

We calculated the magnitude of stress coefficients by a somewhat different method.

A known equation permits calculating of stresses upon glazing and enameling:

$$\sigma = E(t - t')(\alpha_1 - \alpha_2)(1 - 3k + 6k^2)$$

$t - t'$ being the temperature difference, $\alpha_1 - \alpha_2$ the difference in c.l.t.e., k - a coefficient representing the ratio of the thickness of the surface layer and the sheet, respectively, and E - Young's modulus.

We used this equation for calculating the stresses produced by ion exchange.

*Numbers in the margin indicate pagination in the foreign text.

**Composition (wt%) 71.4 SiO_2; 1.2 Al_2O_3; 7.9 CaO, 3.0 MgO; 16.2 Na_2O; 0.2 SO_3.

***The layers were removed by pickling in 10% HF solution.

The values α_1 and α_2 were calculated by Appen's method, (under conditions of equimolecular exchange of sodium and lithium). In this case $\alpha_1 = 96.5 \cdot 10^{-7}$ degree^{-1} (for sodium glass) and $\alpha_2 = 78.4 \cdot 10^{-7}$ degree^{-1} (for lithium glass). Assuming that, with some degree of error, E = 7100 kg/mm^2, k = 0.08 for both glasses, and that the difference t - t' = 460°C, we obtain the value σ = 4 kgf/mm^2, which agrees satisfactorily with experimental values.

A similar calculation for glass containing 8 - 18 wt% Na_2O indicates a nearly identical magnitude of the stress coefficient. Nevertheless, an optimum concentration of Na_2O exists, permitting the achievement of a maximum increase in strength in the shortest time. Thus the strength and thermal stability of VVS glass of the Dzerzhinski plant was increased 2 - 2.5 times by means of a relatively short treatment (50-60 min). /2030

Recently drawn glass of 2.8 mm thickness was used to cut 60 x 60 mm samples. The strength was determined on the WPM tensile tester, using a technique developed on paper [3]. All samples were assigned to three groups: 1 - initial glass, 2 - thermally treated glass, and 3 - glass strengthened by the ion exchange method*. The results are presented in Figure 2 by the corresponding curves of strength distribution.

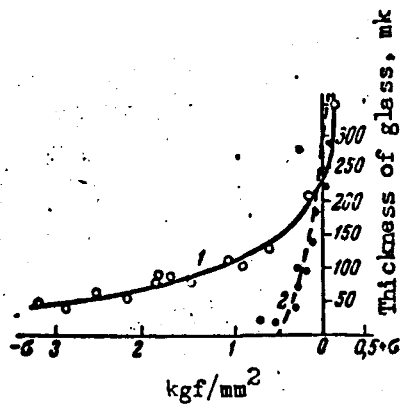

Fig. 1. Diagrams of Stress Coefficients (1) and Tempering Stresses (2)

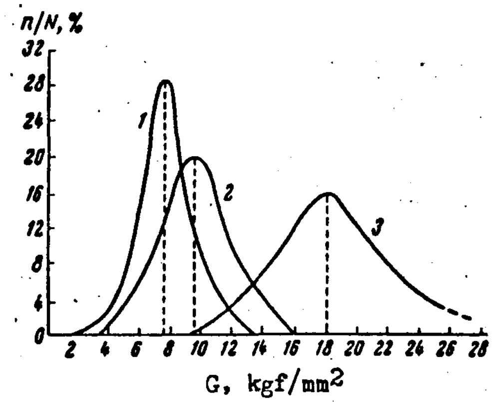

Fig. 2. Strength Distribution of Glass after Ion Exchange

1 - initial glass; 2 - semitempered; 3 - strengthened by the ion exchange method.

The dotted part of curve 3 indicates the estimated strength of samples which were not destroyed at the maximum load on the indicated apparatus.

In glass containing less than 7 wt% R_2O, diffusion of alkali cations does not occur to a significant extent, since they all have extensive stability in the silicon oxide groups, and a very high E_a (activation energy) is required for the initiation of ion exchange. We studied the long-standing treatment of alkali-free 13-B** glass in lithium salts. As expected, several hours of treatment of

*Every group comprises 70 samples.
**Composition (wt%): 63.5 SiO_2, 15.5 Al_2O_3; 2 Na_2O; 13 CaO, 4 MgO.

this glass in the melt at 700°C was not sufficient for formation of an unidentifiable diffusion layer. An increase in mechanical strength was also not detected in samples of 13-B glass, treated in the eutectic melt of lithium and potassium sulfates (treatment time 60 min).

Borosilicate alkaline glass can be hardened by ion exchange if the B_2O concentration does not exceed 2 - 4 wt%. This can be explained primarily by the higher packing density of the structure of all glasses containing B_2O_3, which causes a decrease in ion mobility. Moreover, the magnitude of the c.l.t.e. factor is smaller for borosilicate glass than for silicate glass, so that the difference $\alpha_1 - \alpha_2$ is small.

The method of ion exchange appears to be very interesting and promising /2031
for the strength increase of aluminosilicate glass. If such glass contains a sufficient amount of Na_2O or K_2O, treatment in lithium salts causes the exchange of Na^+ to Li^+ or K^+ to Li^+. Since in glass of this type the Si^{4+} ions are partly replaced by Al^{3+}, the small lithium ions must fill in the voids of the structure in order to preserve the electroneutrality. The presence of a surface layer, capable of forming after thermal treatment, β-spodumene or β-eucryptite with negative c.l.t.e., considerably increases the $\alpha_1 - \alpha_2$ difference.

The realization of stress coefficients for silicate alkaline glass is only possible if the surface is not destroyed during the treatment.

Because of the presence on the initial glass surface of all kinds of cracks, micro- and macrodiscontinuities, the diffusion exchange of Na^+ to Li^+ does not proceed homogeneously over the contact face between glass and melt. Channels and depressions may form in the glass, and, in this manner, the process of diffusion also develops. The formation of depressions causes an increase in the surface area, and, ultimately, an increase in the adhesion of glass and melt. On cooling, the glass develops a rough surface with cuts and cohesion cracks. The electron micrograph of the surface of such glass is shown in Figure 3a*. If alkali metal bisulfate additions are used in the melt [4], the surface of the treated glass is no different from the initial material, and all nonuniformity and roughness disappears (Fig. 3b).

We studied the processes occurring on the interface glass - melt with additives - and we explained the cause of the bisulfate effect, including the regeneration and even slight improvement of the glass surface.

Since the introduction of additives occurs at a comparatively high temperature, the unstable bisulfates (e.g., of potassium) decompose immediately into pyrosulfate and water:

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \quad (1)$$

*Carried out by N. M. Vaysfel'd on a "Tesla" microscope.

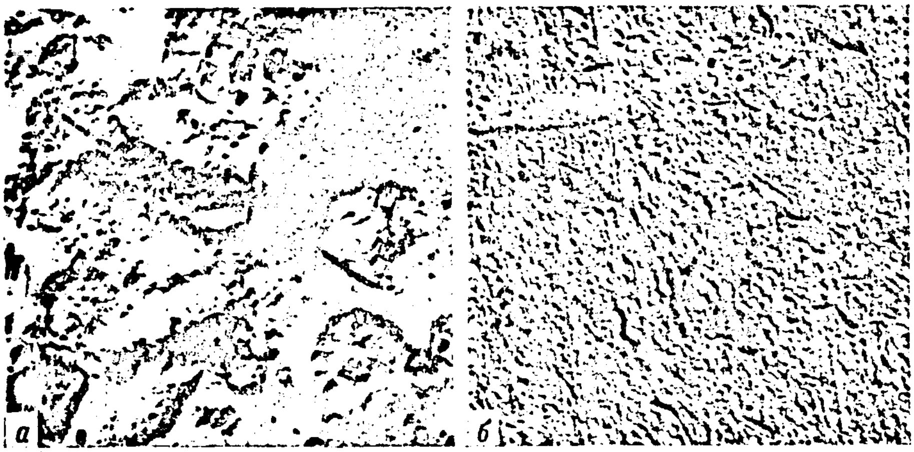

Fig. 3. Electron Micrographs of the Surface of Treated Glass:
a - without additives; b - with additives

Pyrosulfate is also unstable:

$$K_2S_2O_7 \rightarrow SO_3 + K_2SO_4 \tag{2}$$

The double salt $K_2SO_4 \cdot KHSO_4$, which later decomposes to potassium sulfate, sulfurous gas, and water, shows greater stability at the treatment temperature. The highly active water formed by these reactions can dissolve silica, i.e., cause cleavage of Si-O bonds and transform silica from skeleton into molecular form. /2032

The appearance of the silica hydrate and the presence of alkali metal sulfates make feasible reactions which form silicates of lithium, sodium and potassium. The initial temperature for these reactions is 1100-1200°C [5-6], but the presence of highly active water in the melt favors the formation of silicate in the temperature region of 580-600°C [7-8], corresponding to the softening of the glass:

$$(Me)_2SO_4 + H_2O + nSiO_2 \rightarrow (Me)_2O \cdot nSiO_2 + H_2O + SO_3. \tag{3}$$

A factor contributing to the feasibility of this reaction is the lithium silicate glass composition of the surface layer, with a softening point that is 60° lower than the treatment temperature. This is actually a highly viscous liquid.

Upon the interaction of silicates and sulfates of alkali metals we observe the limited mutual solubility of these salts and, as a consequence, the phenomenon of liquefaction. Two immixable liquids are formed, which have an extremely small degree of surface tension, and a boundary which represents an ideal plane. The distribution that is valid for immixable liquids determines the normal diffusion process of Na^+ from the glass and of Li^+ into the glass.

An additional result of these processes is that the surface defects disappear and the strength of the treated glass increases markedly.

CONCLUSIONS

The stress coefficients in glass resulting from ion exchange were determined and calculated experimentally. Corresponding results for both methods were obtained.

Curves of strength distribution for the initial and the treated glass were plotted and the strength of the glass after ion exchange was shown to exceed the initial value by 2-2.3 times.

The advantages of the application of the ion exchange method for the fortification of aluminosilicate glasses were enumerated.

The mechanism of the additive activity of alkali metal bisulfates was explained.

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